

Study of Thermal Behavior Of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in N_2 Atmosphere Using TGA.

SAA Sajadi*, and M Khaleghian.

Sharif University of Technology, Institute of Water & Energy, P.O.Box 11155-8639 Tehran, Iran.

Research Article

Received: 07/01/2014
Revised: 13/03/2014
Accepted: 16/03/2014

*For Correspondence

Sharif University of Technology,
Institute of Water & Energy,
P.O.Box 11155-8639 Tehran,
Iran.

Keywords: Chromium(III) nitrate,
TG, XRD.

ABSTRACT

Using a technique of thermogravimetry and under N_2 gas atmosphere from 25 to 600 °C, the thermal behavior of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was studied. The received products were investigated by XRD. Depending on the conditions of reaction (temperature, heating rate, mass of sample, surrounding atmosphere) thermal decomposition leads to chromium oxides Cr_2O_3 , different size and porosity or specific area of the forming grains. Calculations related to mass loss were also reported.

INTRODUCTION

Due to their chemical and physical characteristics, chromium compounds are used in a wide variety of industries all over the world [1,2,3,4,5,6]. One of the most important characteristics of the chromium concerns its reactions to acids and bases as well as to air, a process known as oxidation. Some are the end product of a desired process but most of them are undesired byproducts known as disturb compounds [7,8,9].

Chromite is one of the most significant compounds used in steel industries [8,9,10]. The morphology of these compounds was also studied [11]. Earlier works showed that two or three step reduction pathway of unsupported CrO_3 is or may be accompanied by simultaneous decomposition of intermediate CrO_x phases (Cr_3O_8 and Cr_5O_{12}), which are eventually transformed into crystalline Cr_2O_3 at about 500 °C [12,13] of magnitude higher than the parabolic oxidation constant. Other Experiments demonstrated that the presence of nitrogen in the substrate is always a precursor to breakdown of the oxide layer and does not result from diffusion through the Cr_2O_3 Layer [14]. The present research intended to investigate the thermal properties of chromium nitrate under different temperature conditions.

EXPERIMENTAL

Materials and equipments

Chromium nitrate was purchased from Merck co., Darmstadt, Germany, article no 2481.0250.

XRD: X-Ray diffractometer STOE (Germany), Model: D-64295.

TG & DSC: Thermogravimeter, / Differential Scanning Calorimeter, coupled with a TA processor, TGA/DSC1. Mettler-Switzerland.

Atomic Absorption Spectrometer, Spectra AA – Varian 220.

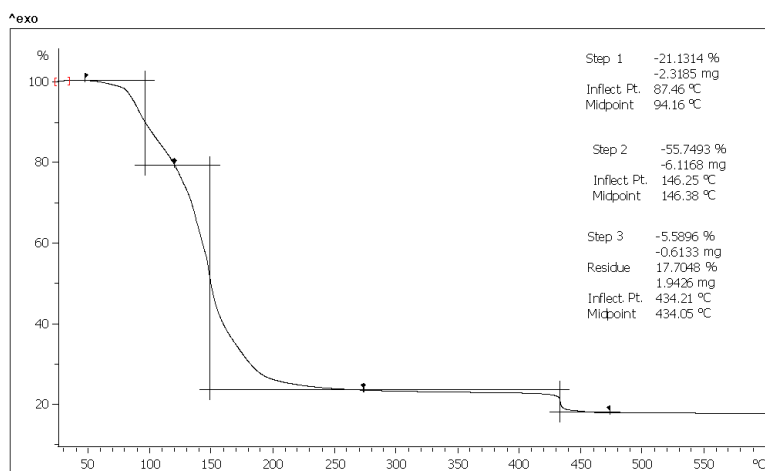
Spectrophotometer, Shimadzu, UV.

TG analysis

A sample of $\text{Cr}(\text{NO}_3)_3$ was placed in a standard alumina 70 μl crucible and weighed accurately (10.9586 mg) using a microbalance. Special equipment was used to seal the sample. The sealed crucible was placed in the

TG/DSC equipment and its temperature was raised from 25 to 600 °C, with a heating rate of 10 °C min⁻¹, under N₂ gas atmosphere. TG curve of this sample are represented in Fig. 1.

Figure 1: TG diagram of Cr₂(NO₃)₃ in N₂ atmosphere.



X-ray powder diffraction

The product from TG experiment was prepared for X-ray and it was exposed to CuK_{α1} radiation for 2 h. Figure 2 shows the XRD diagram of the compound Cr₂O₃ (end product).

RESULTS AND DISCUSSION

Thermal investigations of Cr(NO₃)₃

The TG curve of thermal decomposition of Cr(NO₃)₃ in N₂ atmosphere is shown in Fig. 1. The curve shows the mass loss (vertical axis) of Cr(NO₃)₃ in N₂, while horizontal axis shows temperature increase.

So one can better differentiate between the steps of the thermal decomposition. The results indicate that thermal decomposition consists of three steps in the temperature range of 25–600 °C, these results are summarized in table 1.

The first step takes place between 48–120 °C. This phenomenon is the decomposition of the starting compound and loss of H₂O. Spectroscopic quantitative analysis in this study also corroborates this finding. The computed stoichiometry of decomposition products are in good agreement with experimental results (quantitative and percent decrease in mass).

Table 1: results from the thermal investigations of Cr₂(NO₃)₃ in temperature range 25-600 °C in N₂ atmosphere.

Phase No.	Start temperature [°C]	Turning point [°C]	End temperature [°C]	Mass loss [mg]	Mass loss [%]
1	47.8	87.5	120.2	2.318	21.13
2	120.2	146.3	274.4	6.117	55.75
3	274.4	434.2	475.2	0.613	5.59

First step of decomposition (47.81–120.18 °C)

A heating rate of 10 °C min⁻¹ was chosen to determine more information on what is taking place in this temperature range. The experiment was accomplished in the N₂ atmosphere with a constant gas flow of 30 ml. min⁻¹.

As can be inferred from the results of the Fig. 1, the first phase of (decomposition) pyrolysis reaction of Cr(NO₃)₃·9H₂O occurs in the range of 48–120 °C. Concerning the case of Cr(NO₃)₃, the separation of H₂O was also observed. Investigation of TG curve N₂ atmospheres for this step indicates the presence of the process i.e. loss of H₂O.

By subtracting the experimentally determined quantity of materials (by spectrometric quantitative analysis) from the entire amount of mass loss (21.13%).

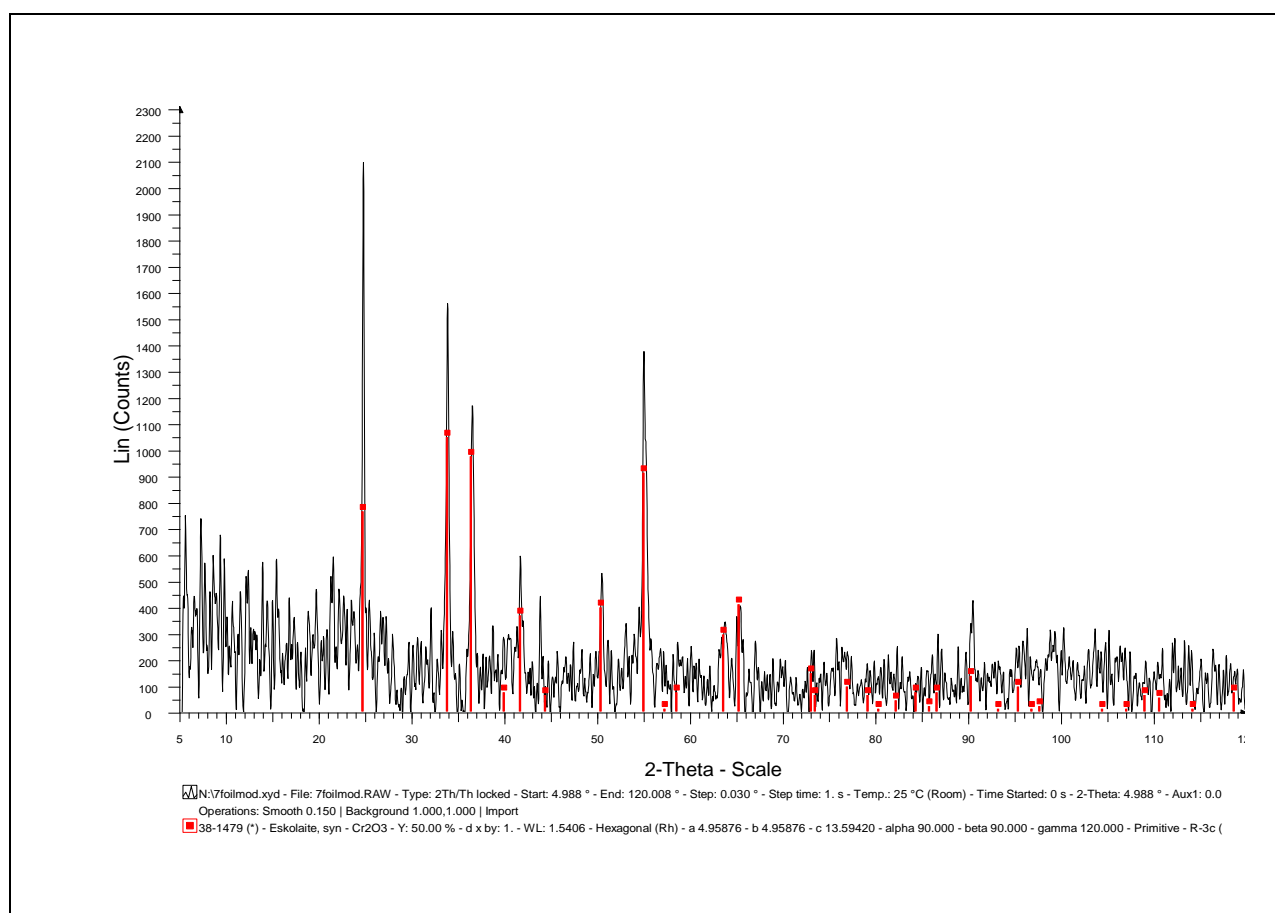
Second step of decomposition (120.18-274.35 °C)

The experiment results show that the product lost about 55.75% of its mass within the range 120–274 °C. The experiment was accomplished in the N₂ atmosphere with a constant gas flow of 30 ml. min⁻¹. The X-ray analysis supplied an amorph XRD diagram. The evaluation of the results as well as spectrometric analysis confirms the brutto formula: CrO_{2.6}.

Third step of decomposition (274.35-475.15 °C)

The experiment results show that the product lost about 5.59% of its mass within the range 274–475 °C. The X-ray analysis supplied a XRD diagram identical to Cr₂O₃ (fig. 2). The evaluation of the results as well as spectrometric analysis confirms the brutto formula: Cr₂O₃.

Figure 2: XRD diagram of Cr₂O₃ (end product) at 600°C.



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